◆ Scientific
Research

Alkaline Earth (Ca) and Transition Metal (Ni) Doping on the Transport Properties of $Y_{1-x}Ca_xBa_2(Cu_{1-y}Ni_y)_3O_{7-\delta}$ Superconductors

Dinesh Varshney[1,2], Arvind Yogi[1], Neha Dodiya[1], Irfan Mansuri[1]

[1]*School of Physics, Vigyan Bhavan, Khandwa Road Campus, Devi Ahilya University, Indore, India*
[2]*School of Instrumentation, USIC Bhavan, Khandwa Road Campus, Devi Ahilya University, Indore, India*
E-mail: vdinesh33@rediffmail.com, vdinesh33@gmail.com

Abstract

We report the results of *dc* resistivity, *ac* susceptibility, and thermopower study of partial substitution at Y (*A* site by Ca) and at Cu (*B* site by Ni) polycrystalline superconductors. The iodometric analysis reveals that the oxygen deficiency, δ, for $YBa_2Cu_3O_{7-\delta}$ (S-I), $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (S-II), $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (S-III) and $Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{7-\delta}$ (S-IV) samples are 0.16, 0.30, 0.39 and 0.29 respectively. The x-ray powder diffraction pattern indicates that all samples are in orthorhombic phase. The *dc* resistivity, *ac* susceptiblity and the thermopower measurements shows that the divalent Calcium doping at the trivalent Y site and transition metal Ni doping at Cu site causes a suppression of the superconducting transition temperature (T_c) from 89 to 81 K. The *ac* susceptibility confirms the ferromagnetic to antiferromagnetic phases at a defined T_c. The room temperature *S* value increases for Ca substituted $YBa_2Cu_3O_{7-\delta}$ while to that it decreases for $Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{6.71}$. The above feature is an indicative of enhanced number of mobile holes for the Ca doped $YBa_2Cu_3O_{7-\delta}$, while to that the charge carrier density is reduced in simultaneous *A* (Ca) and *B* (Ni) site doped sample.

Keywords: Y-Based Superconductors, Doping Effect, Transport Properties

1. Introduction

Both alkaline earth and transition metal substitutions in cuprate superconductors are important for the phenomenon of superconductivity. The presence of magnetic impurities with variable concentration of carriers can cause changes of transport and electronic properties of the bulk system. All cuprate superconductors transformed from anti-ferromagnetic insulators to superconductors, and then to metals for enhanced doping. Thus the substitutional effects in the host compounds provides key insights into the electronic properties, phases, active phonon modes and symmetry of high-T_c superconductivity and has been a major focus of high-T_c research in superconductors, since its discovery [1].

The $YB_2Cu_3O_{7-\delta}$ (YBCO) is an ideal superconductor and much research activities are focused mainly to investigate substitutional effects at Y (*A*) [2-5] site. The partial substitution of Y^{3+} by Ca^{2+} in YBCO changes the carrier concentration and influences the charge transfer from the Cu-O chains to the conducting CuO_2 layers. Ideally, the Oxygen induces superconductivity in Ca-free YBCO while Ca does similarly in oxygen-deficient YBCO. The optimal value for oxygen doping of YBCO is for δ = 6.92 with a T_c of about 90 K. The substitution of alkaline earth metals at *A* site suppresses the superconducting T_c from 90 to 80 K and has been a subject of immense importance.

On the other hand, the presence of transition metal impurities at Cu site (*B*) in $YBa_2Cu_3O_{7-\delta}$ cuprates as well increased oxygen deficiency further suppresses the transition temperature (T_c) [6-11]. Less attention has been paid on simultaneous partial substitution of divalent alkaline earth at Y site (*A*) and transition metal impurity at Cu site. It is now established that high-T_c cuprates as $YBa_2Cu_3O_{7-\delta}$ show a large number of interesting features that includes antiferromagnetic, pseudogap, marginal Fermi liquid and ordinary Fermi liquid phases in addition to the superconducting phase, apart from the changes in the superconducting transition temperature T_c [12,13]. It

is worth to comment that *A* and *B* site doping in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors will lead to an understanding of the effects of pair breaking, local moments, hole doping, ion size effects and disorder on the superconducting condensate.

The transport measurements as *dc* electrical resistivity and thermopower are powerful probes to investigate the electronic states and phases of the host as well of the partially substituted YBCO either at *A* or at *B* site. It is inferred from the resistivity measurements that with the enhanced Ca doping at Y site, the resistivity of the samples decreases significantly [3,4]. Furthermore, Ni atoms substituted for Cu in YBa$_2$Cu$_3$O$_{7-\delta}$ the resistivity for minimal doping decreases as compared to the parent compound, while to that for enhanced doping (50%) the resistivity increases [7]. Substitution of Cu with metallic elements should produce substantial changes in the superconducting T_c, which is also reflected in the transport properties. It is worth to mention that no systematic effort has been made to study the simultaneous substitutional effects in YBa$_2$Cu$_3$O$_{7-\delta}$ with both *A* and *B* site doping.

The thermopower measurement is a technique that gives information about charge carriers. The YB$_2$Cu$_3$O$_{7-\delta}$ superconductor contains both two-dimensional CuO$_2$ planes and one-dimensional CuO chains. We may refer to the work of Bernhard and Tallon [14], who investigated the thermopower of polycrystalline Y$_{1-x}$Ca$_x$B$_2$Cu$_3$O$_{7-\delta}$ [$0 \leq x \leq 0.2$ and $0.04 \leq \delta \leq 0.98$]. The partial substitution introduces additional hole carriers into the CuO$_2$ planes and makes the YBCO system access far into the overdoped regime [15]. The measured thermopower decreases almost linearly with temperature and a room temperature value of $S \sim 1$ - 2 μV/K is documented and is argued for the CuO$_2$ plane contribution. We must mention that no result has been documented in the literature about thermopower for Ni doping at Cu site in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors. Henceforth, it is the purpose of the present paper to investigate the effect of transport properties on the simultaneous substitutional effects in YB$_2$Cu$_3$O$_{7-\delta}$ superconductors.

The ion size effects and disorder on the superconducting state are substantial in YBCO superconductors and with these motivations, we aimed at the understanding of transport properties of both A [divalent Ca ($4s^2$) at the trivalent Y ($4d^1 5s^2$)] and B [Ni ($3d^8 4s^2$) at the Cu ($3d^{10} 4s^1$)] site substitutions in Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$(YCBCO) and Y$_{1-x}$Ca$_x$Ba$_2$Cu$_{3-y}$Ni$_y$O$_{7-\delta}$ (YCBCNO) superconductors. We must mention that the individual effects have been reported earlier in the literature but a simultaneous effect of the Ca substitution and Ni doping has not been investigated. We perform the *dc* resistivity, *ac* susceptibility, and thermopower measurements of YBa$_2$Cu$_3$O$_{7-\delta}$ (S-I), Y$_{0.9}$Ca$_{0.1}$Ba$_2$Cu$_3$O$_{7-\delta}$ (S-II), Y$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_3$O$_{7-\delta}$ (S-III)

and Y$_{0.9}$Ca$_{0.1}$Ba$_2$ (Cu$_{0.99}$Ni$_{0.01}$)$_3$O$_{7-\delta}$ (S-IV) superconductors to delineate the substitutional effects both at *A* and *B* sites.

2. Experimental Details

Polycrystalline samples of YB$_2$Cu$_3$O$_{7-\delta}$ (YBCO), Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$(YCBCO) and Y$_{1-x}$Ca$_x$Ba$_2$Cu$_{3-y}$Ni$_y$O$_{7-\delta}$ (YCBCNO) [S-I – S-IV] were prepared for the experiments conducted by the solid-state ceramic route [16]. Powders of Y$_2$O$_3$, BaCO$_3$, CaCO$_3$, Fe$_2$O$_3$, and NiO in the stoichiometric ratios were mixed and annealing at temperatures (850°C, 900°C) for 24 hours with intermediate grindings. The pellets were annealed at 950°C for 48 h in Oxygen atmosphere. The samples are cooled in oxygen at the rate of 5 to 10 C per minute. A slow with preferably a long anneals enable to have a proper stoichiometry. The x-ray diffraction (XRD) measurements were carried out with Cu Kα radiation using a Rigaku powder diffractometer equipped with a rotating anode scanning (0.01 step in 2θ) over the angular range 10° - 80° at room temperature generating x-ray by 40 kV and 100 mA power settings. For finding oxygen content we perform the improved iodometric titration reported [17].

The *dc* resistivity and thermo power measurements of all prepared samples (SI-SIV) have been done to 10 - 300 K. The *dc* resistivity measurements using four-probe method. Indium contacts are made on the polished surface of the sample. The sample is in the form of a rectangular rod. The SI temperature controller, Schlumberger multimeter and Advantest current source is used for the measurement. A vacuum of the order of 10^{-5} mbar was maintained in the chamber with the help of turbo molecular pump assembly with silicon diode as the sensor. The *ac* susceptibility measurements were carried out using home made setup [18]. In the critical region, the temperature was controlled to an accuracy of 0.01 K using commercial Lakeshore controllers DRC93CA and 340.

3. Results and Discussion

The XRD patterns of YBa$_2$Cu$_3$O$_{6.84}$ (S-I), Y$_{0.90}$Ca$_{0.10}$Ba$_2$Cu$_3$O$_{6.7}$ (S-II), Y$_{0.80}$Ca$_{0.20}$Ba$_2$Cu$_3$O$_{6.61}$ (S-III) and Y$_{0.9}$Ca$_{0.1}$Ba$_2$(Cu$_{0.99}$Ni$_{0.01}$)$_3$O$_{6.71}$ (S-IV) are shown in **Figure 1**. These are indexed in the orthorhombic phase and the deduced lattice parameters are illustrated in **Table 1**. The above lattice parameters are consistent with the earlier reports and corresponds to space group P*mmm* [3,7]. It is inferred that the cell volume increases as Ca doping is partially enhanced at Y site, it further decreases for Ni doping at Cu site. The oxygen content in prepared samples is determined by the improved iodometric titration method [17]. We find the value of δ= 0.16, 0.30,

Table 1. Lattice parameters, cell volume and oxygen content of YBCO superconductors.

S. No.	Sample details	a (Å)	b (Å)	c (Å)	V(Å^3)	δ
1.	$YBa_2Cu_3O_{7-\delta}$ (SI)	3.8067	3.8821	11.6789	172.59	0.16
2.	$Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (SII)	3.8328	3.8764	11.7484	174.551	0.30
3.	$Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (SIII)	3.8369	3.8784	11.7365	174.651	0.39
4.	$Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{7-\delta}$ (SIV)	3.8289	3.8864	11.6372	173.17	0.29
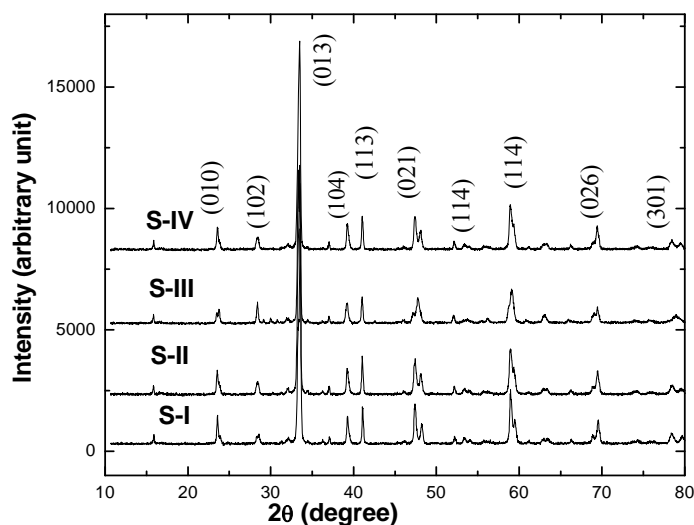
Figure 1. The x-ray diffraction pattern for samples S-I ($YBa_2Cu_3O_{6.84}$), S-II ($Y_{0.90}Ca_{0.10}Ba_2Cu_3O_{70}$), S-III ($Y_{0.80}Ca_{0.20}Ba_2Cu_3O_{6.61}$) and S-IV ($Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{6.71}$).

0.39 and 0.29 for S-I to S-IV, respectively. We note the prepared polycrystalline samples are single phase and the oxygen content as determined from the Iodometric analysis is consistent with the earlier findings [3].

The experimental data for *dc* resistivity of all these samples are illustrated in **Figure 2**. The superconducting transition temperature T_c of samples S-I to S-IV is documented in **Table 2**. It is noticed that the T_c decreases with the increased Ca doping at Y site and further decreases with the substitution of Ni at Cu site. The above is attributed to the fact that the substitution of Ca^{2+} for Y^{3+} in $YB_2Cu_3O_{7-\delta}$ (YBCO) generates holes. The Ca substitution at Y site leads to counteract the hole-filling effect of oxygen vacancies, and the result is a significant increase in conducting hole concentration. The measured values of transition temperature T_c are comparable to the reported data [14] for parent as well as Ca and Ni doping. Furthermore, above T_c, we have observed metallic behavior for all prepared superconductor samples. It is argued that in $Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{6.71}$ the transition metal ions (Ni) are distributed nearly equal between Cu (1) chain and Cu (2) plane sites [11]. The transition metal Ni ions act as hole filling agent and hence shows sharp transition at superconducting state with minimum oxygen deficiency as compared to the parent $YB_2Cu_3O_{7-\delta}$ superconductor. Later on, the *ac* susceptibility measure-

ments of these samples were carried out to confirm the superconducting T_c as shown in **Figure 3**. It is noticed that all the samples S-I to S-IV superconductors undergo a transition from paramagnetic to diamagnetic phase at a defined T_c. The T_c values were determined from the inflexion points of the χ (T) curves consistent with the previous measurements [3].

The results of thermopower (*S*) measurements for S-I to S-IV are shown in **Figure 4**. The value of *S* at room temperature is found to be positive for all the samples, indicating them to be predominantly hole-type conductors. The measured values of thermopower at room temperature for samples S-I–S-IV are 8.3, 10.6, 19.6 and 7.3 μ V K^{-1}, respectively. These values are consistent with the previously reported values [14]. It is inferred that the value of thermopower at room temperature increases monotonically with increasing Ca *x* for first three samples, implying that the number of mobile hole as carrier increases with increasing *x* in the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ superconductor. The result for $Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{6.71}$ superconductor could not be compared due to lack of data.

4. Conclusions

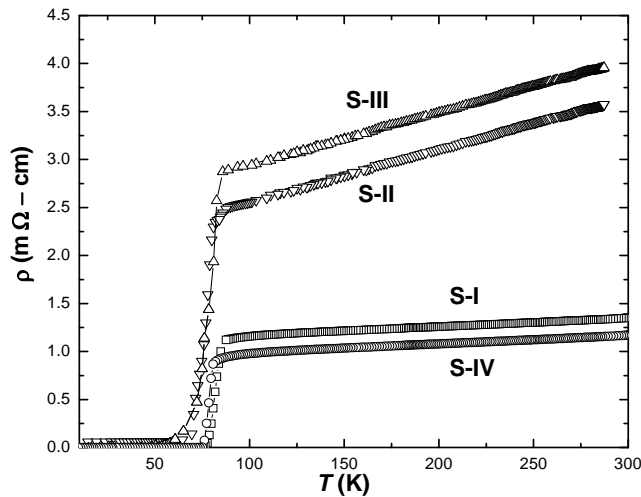The present investigations explore the effect of doping

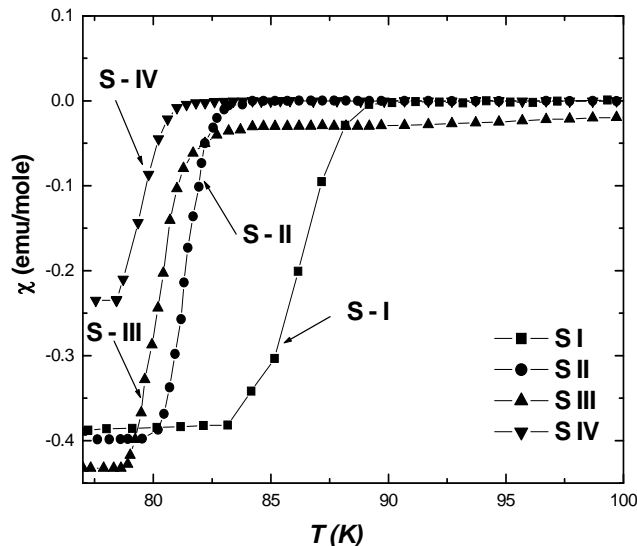**Figure 2. Variation of *dc* resistivity as a function of temperature for samples S-I − S-IV.**

Figure 3. The *ac* susceptibility behavior with temperature for samples S-I − S-IV.

Table 2. Transition temperature T_c, oxygen content (δ) and resistivity ρ values as ρ (300 K) and ρ (T_c) for YBCO superconductors along with previous measurements [14].

S. No.	Sample details	T_c (K)	δ	T_c (K)	δ	ρ (300 K) (mΩcm)	ρ (T_c) (mΩcm)
1.	$YBa_2Cu_3O_{7-\delta}$ (S-I)	89	0.16	93.5 [14]	0.12 [14]	1.35	1.12
2.	$Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ (S-II)	83	0.30	87.9 [14]	0.26 [14]	3.56	2.45
3.	$Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (S-III)	82	0.39	85.5 [14]	0.38 [14]	3.94	2.87
4.	$Y_{0.9}Ca_{0.1}Ba_2(Cu_{0.99}Ni_{0.01})_3O_{7-\delta}$ (S-IV)	81	0.29			1.18	0.91

[non magnetic Ca substitution at Y site and transition metal Ni at Cu site in $YBa_2Cu_3O_{7-\delta}$ superconductors] on the structural, electrical, and magnetic properties. The x-ray diffraction patterns of all samples were indexed in the orthorhombic phase with space group P*mmm*. All the samples were found to be monophasic without any trace of impurity like $BaCuO_3$ or related phases. The cell volume increases as Ca doping increases at Y site, it further

decreases for Ni doping at Cu site. Resistivity and susceptiblity data shows the T_c at 89, 83, 82 and 81 K for S-I − S-IV samples, respectively. Divalent Calcium (Ca) doping at the trivalent (Y) site and transition metal Ni doping at Cu site causes a suppression of the super- conducting transition temperature (T_c) from 89 to 81 K.

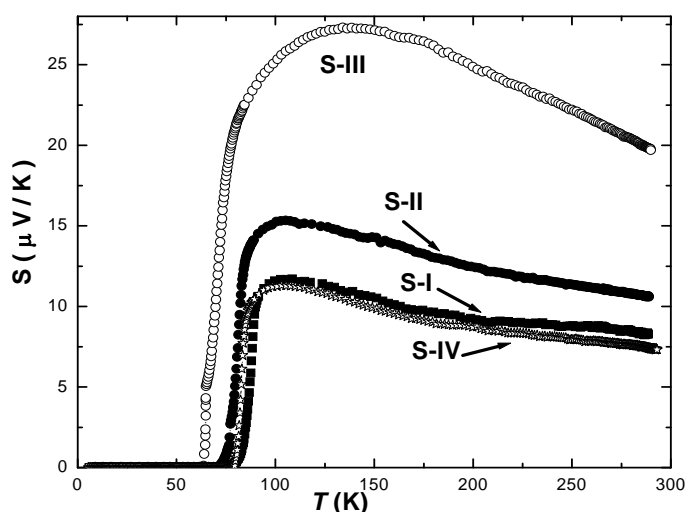Above T_c, the resistivity data for all samples shows metallic behaviour but as Ca doping at Y site (S-II)

Figure 4. Variation of thermopower as function of temperature (*S*) for samples S-I – S-IV.

compare to parent sample (S-I), the magnitude residual resistivity is larger and if further increase the doping of Ca concentration at Y site (S-III), then it also increases. The *B* site Ni doping (S-IV) at Cu, a metallic characteristic is noticed but residual resistivity decreases as compare to the parent sample (S-I). The *ac* susceptibility measurements show a transition from ferromagnetic to antiferromagnetic phase at the well-defined T_c. The room temperature thermopower value increases with increased doping [S-I – S-III] while it decreases for simultaneous doping at *A* and *B* site [S-IV], indicating an enhanced number of mobile holes for first three samples and reduced charge carrier for *A* and *B* site doped S-IV sample.

5. Acknowledgements

6. References

[1]   J. G. Bednorz and K. A. Muller, "Possible highTc Superconductivity in the Ba-La-Cu-O System," *Zeitschrift für Physik B*, Vol. 64, No. 2, 1986, pp. 189- 193.

[2]   W Guan, J. C. Chen and S. H. Cheng, "Ion-Size Effect on Transport Properties in $R_{0.9}Ca0.1Ba_2Cu_3O_{7-\delta}$ Systems (R = Tm, Ho, Gd, and Nd)," *Physical Review B*, Vol. 54, No. 5, 1996, pp. 3580-3588. doi:10.1103/PhysRevB.54.3580

[3]   V. P. S. Awana, A. Tulapurkar, S. K. Mallik and A. V. Narlikar, "Role of Ca in Enhancing the Superconductivity of $YBa_2Cu_3O_{7-y}$," *Physical Review B*, Vol. 50, No. 1, 1994, pp. 594-596. doi:10.1103/PhysRevB.50.594

[4]   B. Fisher, J. Genossar, C. G. Kuper, L. Patlagan, G. M. Reisner and A. Knizhnik, "Effects of Substituting Calcium for Yttrium on the Properties of YBa2Cu3O7-δ," *Physical Review B*, Vol. 47, No. 10, 1993, pp. 6054-6059. doi:10.1103/PhysRevB.47.6054

[5]   R. J. Tellon and L. F. Flower, "Stoichiometric $YBa_2Cu_3O_7$ is Overdoped," *Physica C*, Vol. 204, No. 3-4, 1993, pp. 237-246. doi:10.1016/0921-4534(93)91005-G

[6]   G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du and C. L. Chien, "Effect of Transition-Metal Elements on the Superconductivity of Y-Ba-Cu-O," *Physical Review B*, Vol. 35, No. 16, 1987, pp. 8782-8784. doi:10.1103/PhysRevB.35.8782

[7]   J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene and G. H. Hull, "Structural and Physical Properties of the Metal (M) Substituted $YBa_2Cu_{3-x}M_xO_{7-y}$ Perovskite," *Physical Review B*, Vol. 37, No. 13, 1988, pp. 7458-7469. doi:10.1103/PhysRevB.37.7458

[8]   R. L. Neiman, J. Giapintzakis and D. M. Ginsberg, "Transition Temperature and Irreversibility Line of Cobalt-Doped Single-Crystal $YBa_2Cu_3O_{7-\delta}$: The Effect of High-Pressure Oxygen Annealing," *Physical Review B*, Vol. 50, 1994, pp. 16028-16032. doi:10.1103/PhysRevB.50.16028

[9]   J. T. Kim, J. Giapintzakis and D. M. Ginsberg, "Sign Reversal of the Hall Effect in Superconducting YBa2 $(Cu_{1-x}Ni_x)_3O_{7-\delta}$ Single Crystals," *Physical Review B*, Vol. 53, No. 9, 1996, pp. 5922-5826. doi:10.1103/PhysRevB.53.5922

[10] E. R. Ulm and T. R. Lemberger, "Sign Reversal of the Hall Effect in Superconducting $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ Single Crystals," *Physical Review B*, Vol. 53, No. 9, 1996, pp. 11352-11355. doi:10.1103/PhysRevB.53.11352

[11] B. D. Padalia, S. J. Gurman, P. K. Mehta and O. Prakash, "Extended X-Ray Absorption Fine-Structure Studies of 3d Ions in $YBa_2(Cu_{1-x}M_x)_3O_7$ − delta (x < or = 0.10; M Identical to Mn, Fe, Co, Ni and Zn)," *Journal of Physics*:

Condensed Matter, Vol. 4, No. 33, 1992, p. 6865.
doi:10.1088/0953-8984/4/33/001

[12] M. A. Kastner, R. J. Birgeneau, G. Shirane and Y. Endoh, "Magnetic, Transport, and Optical Properties of Mono-layer Copper Oxides," *Reviews of Modern Physics*, Vol. 70, No. 3, 1998, pp. 897-928;

[13] T. Timusk and B. Statt, "The Pseudogap in High-Temperature Superconductors: An Experimental Survey," *Re- ports on Progress in Physics*, Vol. 62, No.1, 1999, pp. 61- 122.

[14] C. Bernhard and J. L. Tallon, "Thermoelectric Power of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$: Contributions from CuO_2 Planes and CuO Chains," *Physical Review B*, Vol. 54, No. 13, 1996, pp. 10201-10209. doi:10.1103/PhysRevB.54.10201

[15] J. R. Cooper and J. W. Loram, "Some Correlations between the Thermodynamic and Transport Properties of High T_c Oxides in the Normal State," *Journal de Phy-*

sique I France, Vol. 6, No. 12, 1996, pp. 2237-2263.

[16] D. Varshney, I. Mansuri and N. Kaurav, "Effect of Electron/Hole Doping on the Transport Properties of Lanthanum Manganites $LaMnO_3$," *Journal of Physics: Condensed Matter*, Vol. 19, No. 24, 2007, p. 246211. doi:10.1088/0953-8984/19/24/246211

[17] W. M. Chen, C. C. Lam, J. F. Geng, L. Y. Li, K. C. Hung and X. Jin, "A New Calculating Formula of Iodometric Titration For High T_c Superconductors," *Physica C*, Vol. 270, No. 1-2, 1996, pp. 155-158. doi:10.1016/0921-4534(96)00497-2

[18] R. V. Krishnan and A. Banerjee, "Harmonic Detection of Multipole Moments and Absolute Calibration in a Simple, Low-Cost Vibrating Sample Magnetometer," *Review of Scientific Instruments*, Vol. 70, No. 1, 1999, pp. 85-91. doi:10.1063/1.1149545